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ECF Kraft Pulp Bleaching Sequence:
Modeling and Effects of Pulping Conditions

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Brightness Development in the Final ClO_2 Stages of an ECF Kraft Pulp Bleaching Sequence: Modeling and Effects of Pulping Conditions

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ABSTRACT

To gain an understanding of the factors that determine bleachability in the final stages of an elemental chlorine-free bleaching sequence, conventional and modified kraft pulps were prepared in the laboratory and bleached in a $D_0(EO)D_1ED_2$ sequence with varied applications of ClO_2 in the D_1 and D_2 stages. After delignification at a constant kappa factor, the extent of D_1 brightening was determined by ClO_2 consumption and pulp type, but not by unbleached kappa number. For a given brightness after the D_1 stage, modified pulping produced pulps that consumed less ClO_2 than conventional pulps. Brightening in the D_2 stage was described by a simple equation relating final brightness to ClO_2 consumed. The parameters in this equation may be interpreted in terms of a brightness ceiling and a rate of approach to the brightness ceiling, termed the D_2 response factor. The brightness ceiling increased with increasing levels of brightness entering the D_2 stage, and was higher for modified than for conventional pulps. The response factor decreased as the entering brightness was increased and was higher for pulps of lower unbleached kappa number.

INTRODUCTION

Kraft pulp bleaching sequences in which Cl_2 has been completely replaced by ClO_2 have grown rapidly in commercial importance (1, 2). Despite this rapid growth, however, there is still much to be learned about the behavior of such sequences with respect to changes in process variables and the relationships between this behavior and the properties of the unbleached pulp. Gaining a more complete understanding of these phenomena is important for at least two reasons. The first is that such knowledge is a prerequisite for identifying and maintaining optimal operating conditions in current operations. In the longer term, however, an understanding of the factors that contribute to bleachability will be needed to gain control of the unbleached pulp properties that determine it. The ultimate goal of research directed along these lines is control of pulping conditions to optimize bleachability.

For this purpose, the term "bleachability" must be more sharply defined than it has been in the past. It has sometimes been used in the same sense as brownstock kappa number, K number, or other indicators of the *amount* of residual lignin in the unbleached pulp. By this definition, a "hard" pulp, containing a relatively large amount of residual lignin, is said to have low bleachability, while low-kappa, "soft" pulps are considered to be highly bleachable. In the context of the objectives outlined above, however, it is more useful to define bleachability in terms of the ease of bleaching pulp containing a given amount of residual lignin to a given target brightness. According to this definition, bleachability is related to the *character* of the residual lignin, not its *amount*.

It is useful to elaborate on this definition by subdividing the bleachability into at least two components. This is because chemical pulp bleaching sequences can be regarded as combinations of a delignifying partial sequence [the D_0 and (EO)stages in the present case] and a brightening partial sequence [the D_1, E, and D_2 stages in the present case]. The effects of pulping conditions on bleachability in the $D_0(EO)$ partial sequence and its relationship to residual lignin structure were the subject of an earlier paper (3). The present paper describes the results of an experimental investigation of bleachability in the D_1ED_2 brightening partial sequence. The pulps studied were prepared from southern pine chips in the laboratory under both conventional and modified kraft pulping conditions. The conditions used for the modified pulps were chosen to simulate those used for extended delignification by the EMCC® process.

EXPERIMENTAL

Kraft Pulping

With one exception, the pulps were prepared at the pilot facilities of Ahlstrom Machinery Inc. in Glens Falls, NY, from chips prepared at the Institute of Paper Science and Technology. The procedures used have been described elsewhere (4). The chips used for all pulps were from a *Pinus taeda* tree cut in North Georgia, USA. Chips prepared from the debarked logs were screened, and the fraction having thickness between 2 and 6 mm. was used. Table 1 lists the conditions used, together with some properties of the resulting pulps.

Table 1. Pulping Conditions and Pulp Properties

	Conventional			Modified		
Init. EA, % NaOH	19.7	19.7	23.2	12.0	12.0	12.0
Cocurrent EA, % NaOH	0.0	0.0	0.0	5.0	5.0	5.0
Max. Temp., °C	170.0	170.0	173.0	157.5	161.0	168.6
H-Factor	1715	2601	4900	1651	2229	4238
Kappa Number	28.0	18.5	9.8	29.1	18.5	14.5
Visc., mPa.s	33.6	17.5		51.8	35.4	18.1
Yield, %	45.9	42.8	39.3	45.6	43.8	40.9

D_0(EO) Bleaching

Duplicate samples of each unbleached pulp were independently bleached in the D_0(EO) partial sequence. The D_0 stage was performed in a Quantum Technologies mixer at 45°C and 10% consistency for 30 minutes at a kappa factor of 0.187±0.005. The (EO) stage was done in a peg mixer at 70°C and 10% consistency for 60 minutes with a charge of sodium hydroxide corresponding to 50% of the total active chlorine (TAC) charge in the D_0 stage. The O_2 pressure was 60 psig initially and was decreased by 12 psi every 5 minutes. The modified pulps delignified somewhat more easily than the conventional ones, as described earlier (3). The data are summarized in Table 2, which shows results averaged over the duplicate samples.

D_1 and D_2 Bleaching

The D_1 and D_2 stages were conducted in sealed Kapak bags at 70°C and 10% consistency for 180 minutes. An amount of NaOH estimated to give a final pH of 4 was added to the pulp at the beginning of the bleaching period. Residual ClO_2 and pH were determined at the end of the bleaching period. The pulp was well washed between stages.

Table 2. D_0(EO) Bleaching Data

	Conventional			Modified		
Unbl. Kappa	28.0	18.5	9.8	29.1	18.5	14.5
D_0 Kappa	11.0	9.6	5.0	11.0	7.5	6.0
TAC/ΔKappa	0.300	0.398		0.309	0.320	0.330
D_0(EO) Kappa	3.8	3.8	2.4	3.3	3.0	2.3
TAC/ΔKappa	0.210	0.234		0.213	0.222	0.230
D_0(EO) Brightness	47.4	49.9		49.8	50.2	53.5

RESULTS AND DISCUSSION

Brightness Development in the D_1 Stage

Each of the D_0(EO) pulps was bleached with ClO_2 at two different levels of applied ClO_2. In many cases, appreciable residual ClO_2 remained at the end of the bleaching period, and there was considerable variability in the residual levels because of variability in final pH. For these reasons the results were analyzed in terms of the amount of ClO_2 actually consumed by the pulp. It is reasonable to assume that the same relationship between ClO_2 consumed and brightness would be obtained under pH conditions that result in lower residual ClO_2 values; in most cases the occurrence of residual ClO_2 could be attributed to chlorite in the spent bleach liquor, formed as a result of the pH being too high. At lower pH, the same consumption would occur at lower charge.

As shown in Figure 1, the modified pulps were more readily bleached to any given brightness. This accounts, in part, for the known lower oxidant requirements of modified pulps (5). The mechanism by which the modified pulps are more readily brightened may be similar to the mechanism by which they are more readily delignified in the D0(EO) sequence. As reported earlier (3), this could be due to a higher content of aryl ether linkages and a lower content of condensed structures.

Brightness Development in the D_2 Stage

Each of the D_0(EOP)D_1 pulps was alkali extracted and then bleached again with ClO_2 at four different levels of ClO_2 applied. Substantial differences in brightness response were observed between pulps, depending on their type (conventional or modified), unbleached kappa number, and brightness after the D_1 stage.

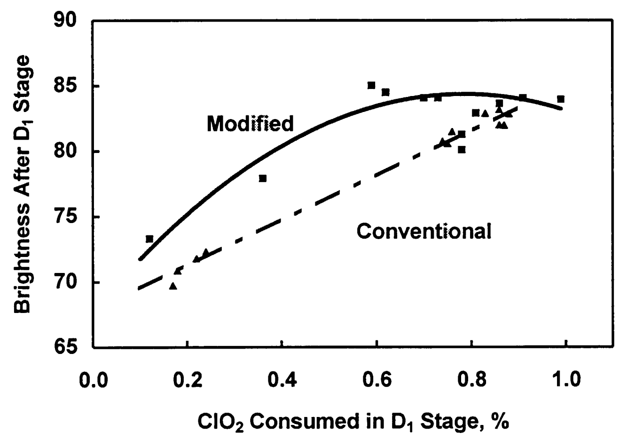

Fig. 1. Modified pulps consume less ClO_2 in the D_1 stage to reach a given brightness in that stage. Squares: modified; triangles: conventional.

Figure 2 illustrates the influence of the D_1 brightness level on the brightness after the D_2 stage. The maximum brightness achievable in the D_2 stage was lower for pulps that had lower brightness after the D_1 stage. Although the data shown in Figure 2 are for conventional pulps, a similar dependence of brightness ceiling on entering brightness was noted when modified pulps were bleached.

At the same entering brightness, however, conventional and modified kraft pulps behave differently in the D_2 stage. The modified pulps exhibit a higher brightness ceiling, as illustrated in Figure 3. This, like their lower chemical demand in the D_1 stage, is an indicator of the inherently easier bleachability of the modified pulps.

Another factor found to influence brightness response in the D_2 stage was the kappa number of the unbleached pulp.

Even though the pulp undergoes much processing between its entry into the bleach sequence and its arrival at the D_2 stage, it appears to "remember" its roots. As Figure 4 shows, the pulps that were initially of low kappa number respond more favorably at low levels of ClO_2 consumption. The effect is illustrated in Figure 4 for modified pulps, but it was also apparent when the conventional pulps were bleached.

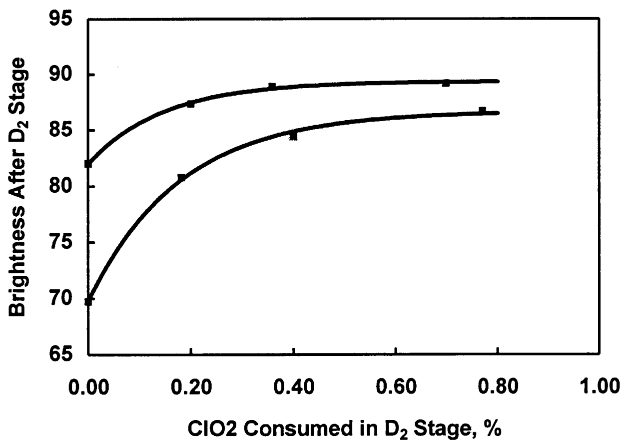

Fig. 2. Bleaching to a higher brightness in the D_1 stage increases the maximum brightness achievable in the D_2 stage. Data shown are for conventional pulps of kappa no. 28.

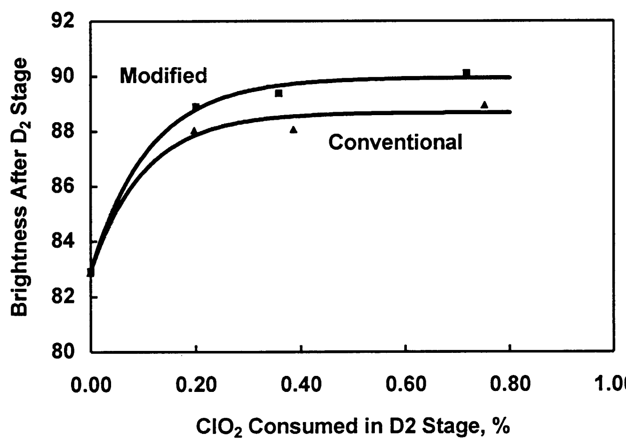

Fig. 3. Modified pulps can be bleached to a higher brightness in the D_2 stage than conventional pulps having the same brightness after the D_1 stage.

A Mathematical Model for D_2 Bleaching

The results presented in Figures 1-4, as well as the results of all of the remaining D_2 bleaching experiments, can be accurately represented by a simple mathematical model. The model consists of the following equation:

$$y = b_0 + b_1[1 - \exp(-b_2x)] \qquad (1)$$

In this equation, y is the brightness of the pulp after the D_2 stage, and x is the charge of ClO_2 consumed. The usefulness of this model derives not only from the fact that it appears to accurately fit the data from all pulps bleached, but also from the fact that physical significance can be attached to each of its parameters. Thus, b_0 is the brightness at a ClO_2 charge of zero, which may be approximated by the brightness of the pulp entering the D_2 stage or leaving the D_1 stage. The second parameter, b_1, is the maximum possible brightness increase relative to b_0 and therefore provides an estimate of the maximum brightness gain that can be achieved. The sum (b_0+b_1) estimates the brightness

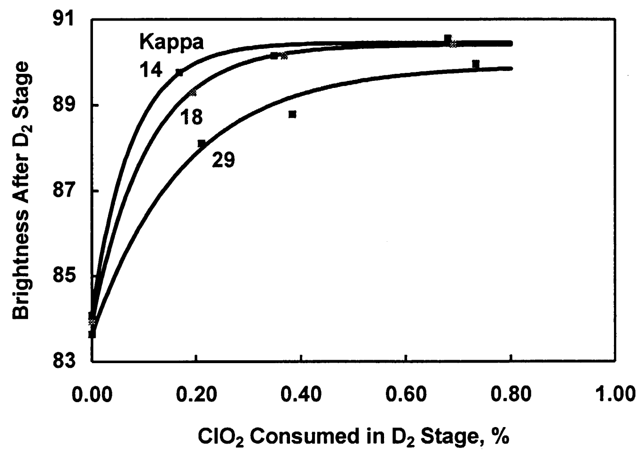

Fig. 4. Decreasing unbleached kappa number increases brightness response in the D_2 stage. Modified kraft pulps.

ceiling, the upper asymptotic limit to the curve and the maximum brightness that can be achieved for a given pulp entering the stage, regardless of how much ClO_2 is consumed. The last parameter, b_2, measures the relative rate of approach to the asymptotic limit. Differentiation with respect to x shows that the initial slope of the curve is given by the product b_1b_2. This represents the responsiveness of brightness to increases in ClO_2 consumption at very low ClO_2 levels; a high value corresponds to a rapid approach to the brightness ceiling. It might be called the D_2 response factor. It is apparent from this discussion that both the brightness ceiling, (b_0+b_1), and the response factor, b_1b_2, are potentially useful measures of different aspects of bleachability in the D_2 stage. Figure 5 illustrates the physical interpretation of the parameters of equation (1).

Factors Affecting the Final Brightness Ceiling

The above model predicts that no amount of ClO_2 will cause the brightness to exceed the brightness ceiling, (b_0+b_1). Since the D_2 stage is normally the last stage in the bleach plant, it is important to understand the nature of the factors that determine the brightness ceiling.

As already illustrated in Figures 2 and 3, two of these factors are the pulp type and the brightness entering the D_2 stage. Figure 6 generalizes these effects by plotting all of the data from this study in terms of the sum of the fitted parameters, b_0 and b_1. The data suggest a linear increase in brightness ceiling with increasing D_1 brightness, and an

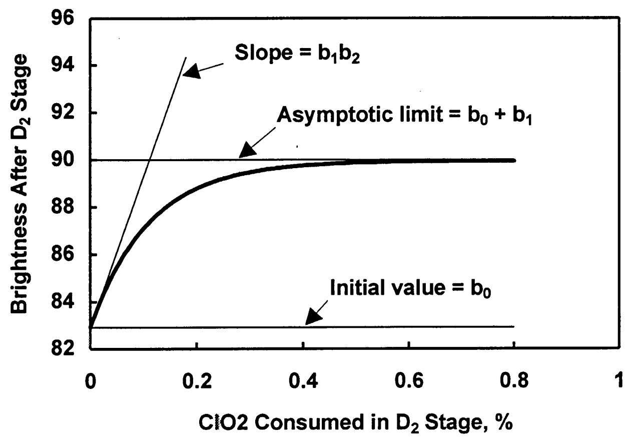

Fig. 5. Graphical representation of equation 1, showing correspondence between parameters in equation and bleachabilitycharacteristics of pulp.

advantage for the modified pulps that is independent of entering brightness. For the same brightness ceiling, the entering brightness of the modified pulps can be five points lower.

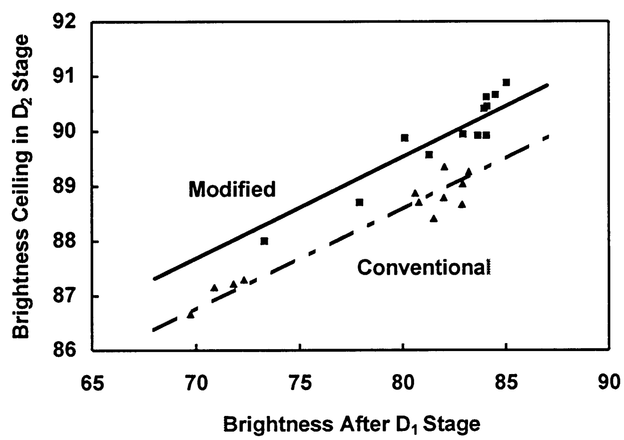

Fig. 6. The maximum brightness achievable in the D_2 stage increases as the D_1 stage brightness is increased. For a given D_1 stage brightness, modified pulps can be bleached to a higher brightness in the D_2 stage.

Brightness Response in the D_2 Stage

As discussed above, the upper asymptotic limit is one important characteristic of the curve that describes the increase in brightness with increasing ClO_2 consumption in the D_2 stage. Another is the initial slope of the curve, which describes the rapidity with which the asymptotic limit is approached. Differentiation of equation (1) with respect to ClO_2 consumed shows that this initial slope is equal to the product of the parameters b_1 and b_2. It has the units of points of brightness increase per unit of chemical charge consumed and may be termed the D_2 response factor or initial D_2 response.

Figure 7 shows how it is affected by entering brightness and unbleached kappa number. Pulps of low unbleached kappa number respond better than high-kappa pulps, and response decreases as the entering brightness increases. There was no evidence for differences in response between conventional and modified pulps.

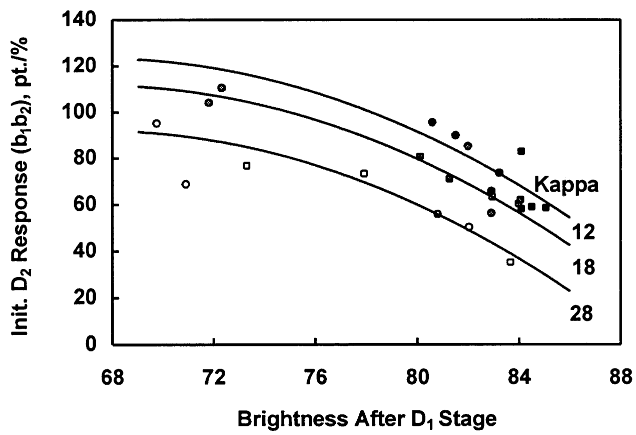

Fig. 7. Initial slope of the D_2 stage brightness curve vs. D_1 stage brightness and unbleached kappa no. Data symbols: open, kappa 10-14; shaded,kappa 18; filled, kappa 28-29; circles, conventional; squares,modified.

SUMMARY AND CONCLUSIONS

Kraft pulp bleachability in ECF sequences may be described not only in terms of ease of lignin removal during the early stages of the sequence, but also with regard to ease of brightening in the later stages. After delignification at a constant kappa factor, the extent of D_1 brightening is determined by ClO_2 consumption and pulp type, but not by unbleached kappa number. Brightening in the D_2 stage may be described by a simple equation relating final brightness to ClO_2 consumed. The parameters in this equation may be interpreted in terms of a brightness ceiling and a rate of approach to the brightness ceiling, termed the D_2 response factor. The brightness ceiling increases with increasing levels of brightness entering the D_2 stage, and is higher for modified than for conventional pulps. The response factor decreases as the entering brightness increases, and is higher for pulps of lower unbleached kappa number. Characterization of bleachability in these terms will facilitate future studies of the relationship between pulping conditions and bleachability, with the ultimate being an ability to predict how any given unbleached pulp will behave in the bleach plant and to maximize bleachability through judicious choice of pulping conditions.

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